PRECISION MEASUREMENTS OF MERCURY 198 WAVELENGTHS

THE UNIVERSITY OF ALBERTA

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A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

FACULTY OF ARTS AND SCIENCE

DEPARTMENT OF PHYSICS

by

ANTON ARTHUR SCHULTZ

EDMONTON, ALBERTA

SEPTEMBER 1958

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ABSTRACT

The vacuum wavelengths of eighteen lines of the Mercury 198 spectrum were measured. A Fabry-Perot interferometer with three different etalon spacers was used. The results agree within experimental error with measurements made by other experimenters, J.M. Blank, W.F.Meggers and K.G.Kessler, and K. Burns and K.B. Adams.

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I INTRODUCTION

Precision measurements in spectroscopy require that there be a standard wavelength (or wavelengths) to which subsequent investigation may be referred. Because it is not always convenient or even possible to use the primary standard, cadmium 6438.4696A, lines from the spectra of various other elements have been proposed as secondary standards; for example, many of the lines of neon and argon are used for this purpose.

In 1940 it was reported by Weins and Alvarez (1) that $^{198}_{80}Hg$ could be excited to emit radiation free from isotopic and hyperfine structure. Furthermore it can be excited at low temperatures and low vapor pressure; hence the wavelengths are determinable to a high degree of accuracy, of the order of 1 part in 5 x 10^7. Various experimenters(2,3,4) have made measurements of these lines. In the present work these measurements are repeated with special emphasis on the ultra-violet portion of the spectrum.

The vacuum wavelengths were determined by means of a Fabry-Perot interferometer crossed with a Hilger E 1 Littrow Spectrograph. The measurements were made with respect to 4 neon visible lines as secondary standards.

II THEORY

1. Fabry - Perot Interferometer

The Fabry - Perot interferometer consists of a pair of transparent plates coated with a partially reflecting, partially transmitting layer of metal. The plates usually are glass, or quartz if the investigation is to be carried into the ultra-violet. The metals used are silver and aluminum because these possess the essential properties, namely, high reflectivity (80-95%) and low absorption, necessary to obtain high resolution with appreciable intensity. Silver is superior to aluminum in the infra-red and visible regions of the spectrum[6] but it has a strong absorption band at 3000 A; hence, for ultra-violet spectroscopy aluminum coated plates are essential. The reflectivity of aluminum begins to decrease considerably at about 2500 A.

The plates of the interferometer are separated by a spacer which is often quartz or invar. These materials are chosen for their low coefficient of thermal expansion to insure stability throughout small temperature variations.

The components of the interferometer are assembled so that the plates are as nearly parallel as possible,

to an accuracy of a fraction of a wavelength of light. The spacer must be of a high quality so that such arrangement is attainable.

A ray of light entering the interferometer in a direction nearly perpendicular to the plates is partly reflected and partly transmitted at each metal surface (fig. 1). The condition for constructive interference is

$$p\lambda = 2\mu t \cos\theta \tag{1}$$

where p is an integer, λ is the wavelength of the light, θ is the angle of incidence, t is the plate separation, and μ is the refractive index of the medium between the plates. If the space between the plates is evacuated $\mu = 1$. Because of the symmetry about the normal to the plates circles of interference maxima and minima, focussed at infinity, will be observed.

2. Calculation of the Fractional Part of the Order Number

An order number P which in general will not be integral is assigned to the centre of the pattern (here $\theta = 0$); P may be written as the sum of an integer Po and a fraction e. Then at the centre of the interference pattern

$$(P_o + e)\lambda = 2t \tag{2}$$

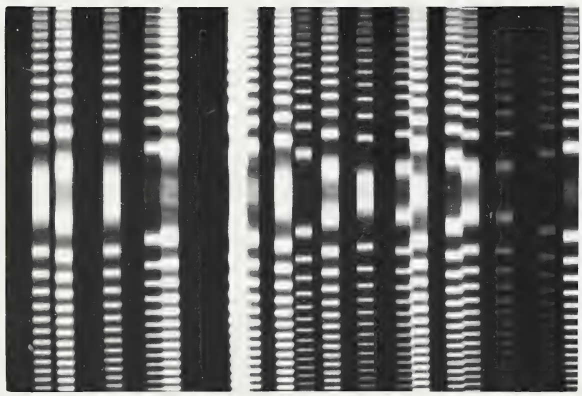

Plate 1. - Typical Interference Pattern

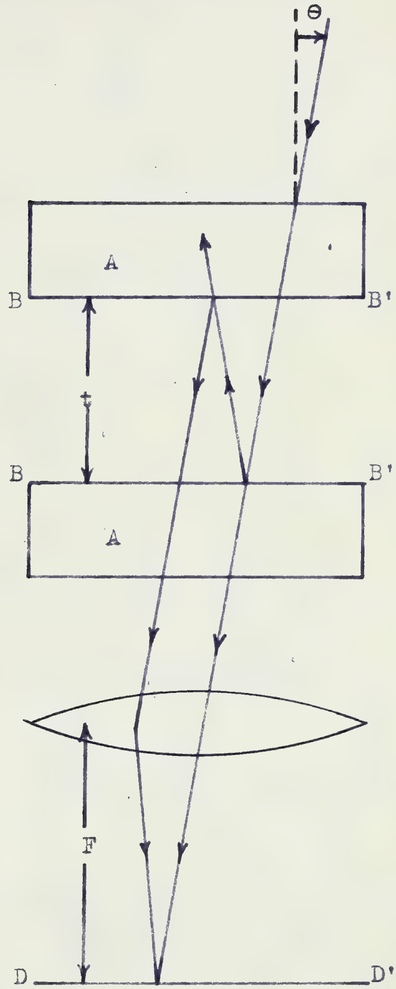

Figure 1. Ray of Light Passing Through Interferometer.

A: etalon plates
BB': metal surfaces
C: convex lens
DD': focal plane of lens

The order number of the n^{th} bright ring is (Po - n) where n = 0,1,2, ..., beginning at the centre of the pattern and counting outwards. Now

$$\cos \theta_n = 1 - \frac{D_n^2}{8f^2} \qquad (3)$$

if $D_n \ll f$, where Dn is the diameter of the n^{th} bright ring as observed in the focal plane of the lens of focal length f. Substitution in equation (1) gives the result

$$2t\left(1 - \frac{D_n^2}{8f^2}\right) = (P_o - n)\lambda$$

But from equation (2)

$$(P_o + e)\lambda = 2t$$

$$\therefore e = \frac{2t}{8\lambda f^2} D_n^2 - n$$

Or $$e = K D_n^2 - n \qquad (4)$$

where K is a constant independent of n.

The fractional portion of the interference order number at the centre of the pattern can be calculated from equation (4). To increase the accuracy of this calculation several diameters are measured and a least squares line is fitted to the data. The normal equations (Appendix I) are

$$je = K \sum_{n=0}^{j-1} D_n^2 - \sum_{n=0}^{j-1} n \qquad (5)$$

$$e \sum_{n=0}^{j-1} n = K \sum_{n=0}^{j-1} n D_n^2 - \sum_{n=0}^{j-1} n^2 \qquad (6)$$

where j is the number of diameters measured. These

equations may be solved for e and K

$$e = \frac{\sum_{n=0}^{j-1} n^2 \sum_{n=0}^{j-1} D_n^2 - \sum_{n=0}^{j-1} n \sum_{n=0}^{j-1} n D_n^2}{j \sum_{n=0}^{j-1} n D_n^2 - \sum_{n=0}^{j-1} n \sum_{n=0}^{j-1} D_n^2} \tag{7}$$

$$K = \frac{j \sum_{n=0}^{j-1} n - \left(\sum_{n=0}^{j-1} n\right)^2}{j \sum_{n=0}^{j-1} n D_n^2 - \sum_{n=0}^{j-1} n \sum_{n=0}^{j-1} D_n^2} \tag{8}$$

In particular for $j = 5$ these equations become

$$e = \frac{3 \sum_{n=0}^{4} D_n^2 - \sum_{n=0}^{4} n D_n^2}{\frac{1}{2} \sum_{n=0}^{4} n D_n^2 - \sum_{n=0}^{4} D_n^2} \tag{9}$$

$$K = \frac{1}{2\left(\frac{1}{2} \sum_{n=0}^{4} n D_n^2 - \sum_{n=0}^{4} D_n^2\right)} \tag{10}$$

An estimate of the accuracy of the value of e is made by computing the standard error of estimate.

$$\text{Standard error of estimate} = \sqrt{\sum_{n=0}^{4} \frac{(e - e_n)^2}{5}} \tag{11}$$

where e_n is computed from equation (4).

A more detailed and complete theory of the Fabry-Perot interferometer is given by Meissner[5] and Tolansky.[6]

3. Calculation of Etalon Separation.

The separation of the interferometer plates must be known to about 1 part in 10^8 if an unknown wavelength is to be calculated to that order of accuracy. To find the separation a standard wavelength (or wavelengths) is measured; secondary standards such as the lines of neon are convenient for this purpose. For the calculation of the separation it is necessary to know:

1) The wavelengths of at least two of the standard lines to an accuracy of about 1 part in 10^8.

2) The fractional parts of the order numbers of the standard lines.

3) An approximate value of the separation (preferably to at least four significant figures).

With two calculating machines the following method may be used to compute the precise value of the separation. An approximate value of P (the interference order number) is computed from equation (2) for two wavelengths, using the exact value of the wavelengths and the approximate value of 2t. The two wavelengths are then set on the calculating machines as constant multiplicands; the order numbers with the measured fractional parts are set on the keyboards as multipliers. Multiplication will give two values of 2t which will probably be different from each other. The integral parts of the order numbers are changed by constant amounts and the multiplications are continued until the two calculated values of 2t agree with each other to about 1 part in 10^8. A third and fourth wavelength are used as a check.

It is usually necessary to follow this procedure only once since the value of 2t does not change appreciably for subsequent exposures with the same etalon spacer.

Several other methods of calculating the plate separation are discussed by Meissner.[(5)]

4. Calculation of Wavelengths.

To calculate the value of an unknown wavelength it is necessary to know:

1) The fractional part of P for the unknown wavelength.

2) An approximate value of the wavelength (5 or 6 significant figures)

3) An exact value of 2t (about 1 part in 10^8).

By equation (2) an approximate value of P is calculated from the exact value of 2t and the approximate wavelength. The measured fractional part is substituted into P and equation (2) is used again to calculate an exact value of the wavelength.

The known approximate value of the wavelength may not be sufficient to determine the integral part of P exactly; as a result P may be incorrect by the amount of some small integer. In this case the observations at a different etalon separation serve as a check and the correct integral portion of the order number is readily established.

5. Phase Change at Reflection.

Upon reflection at a metallic surface a small phase change is introduced between the incident and reflected beams of light. This phase change is a function of the wavelength of the incident light, of the nature of the metal, its thickness and condition. To eliminate the dispersive effect that the phase change has on the cal-

culated values of the wavelength it is necessary to make a correction to each wavelength. With observations made at at least two different etalon separations, it is possible to determine the necessary correction experimentally.

The phase change correction can be made by assuming an apparent change δt in the separation of the etalon plates, and independent of the separation. For two thicknesses t1 and t2 equation (2) may be written

$$P' = \frac{2t_1}{\lambda'} = \frac{2(t_1 + \delta t)}{\lambda} \tag{12}$$

$$P'' = \frac{2t_2}{\lambda''} = \frac{2(t_2 + \delta t)}{\lambda} \tag{13}$$

where λ' and λ'' are the observed wavelengths at thicknesses t1 and t2, respectively, and λ is the true wavelength. The solutions for λ are

$$\lambda = \lambda' + \frac{(\lambda'' - \lambda')t_2}{t_2 - t_1} \tag{14}$$

$$\lambda = \lambda'' + \frac{(\lambda'' - \lambda')t_1}{t_2 - t_1} \tag{15}$$

The choice of etalon spacers is important; choosing two nearly equal separations makes the factors $\left(\frac{t2}{t2-t1}\right)$ and $\left(\frac{t1}{t2-t1}\right)$ large. The error in the wavelength difference $(\lambda'' - \lambda')$ is multiplied by these factors, and hence the error in the phase change corrections will be proportional to them. It is desirable to use at least one large and one small etalon separation.

K.W. Meissner [5] describes more fully this method of applying a correction for phase change; also, A.W. Smith [7] outlines another method.

III APPARATUS

1. General Considerations

The apparatus used in the work was the same, with some minor alterations, as that used by A.W. Smith[7] and R.A. Olafson.[8] A more detailed account of some aspects of the apparatus is given by them.

The Fabry - Perot interferometer used consisted of two quartz plates each aluminized on one surface. The spacers which were available were made of invar. To separate the many lines of the neon and mercury spectra it was necessary to "cross" the interferometer with a spectrograph. The methods of doing this are discussed by Tolansky.[6]

The spectrograph used for this purpose was a Hilger El Littrow Spectrograph with quartz optical components. It was found necessary to redetermine the settings which best focus horizontal lines; the results are given in Appendix II. The entrance slit was opened about $\frac{1}{2}$ mm.

The etalon was situated in a vacuum-tight brass chamber which in turn was immersed in a water bath. The temperature of the bath was thermostatically controlled; a heating element, water-cooled coils, and a stirring mechanism assured that the temperature of the bath was kept constant. By varying the rates of heating and cooling it was found possible to control the length

Plate 2. Components of Interferometer.

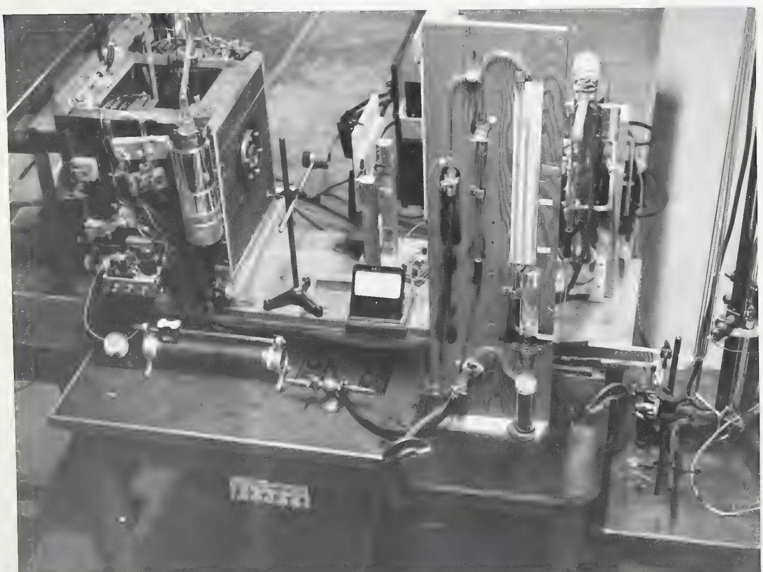

Plate 3. General View of Apparatus.

of the thermostatic cycle. This was adjusted to about 4 minutes, the same length of time as the duration of the neon and shortest mercury exposures. In this way the average temperature during the exposure would be the same as the average temperature over a thermostatic cycle.

A check was kept on the temperature by means of a Beckman thermometer. This instrument was calibrated, but since the temperature does not enter directly into any calculations, only the results of that calibration will be given here:

$$T\ (\pm .006\,^{\circ}C) = 17.054\,^{\circ}C \quad + 1.015\,B$$

where T is the temperature in degrees centigrade and B is the reading of the Beckman thermometer. The method of calibration was the same as that used by A.W. Smith[7] and R.A. Olafson.[8] The average temperature of the bath for each exposure was 21.40 °C.

The thermometer showed variations of .01 °C about the average temperature during one thermostatic cycle. Taking the coefficient of thermal expansion of invar to be $0.9 \times 10^{-6}/^{\circ}C$,[9] this results in a variation of 2×10^{-8} cm. in the length of the etalon spacer. Since this variation is about 1/10 the uncertainty in the measurement of the etalon separation, it may be neglected.

The mechanical vacuum pump used to evacuate the

the etalon chamber was situated at a distance from the main apparatus and mounted on three sets of shock mountings. This permitted continuous pumping of the chamber without the danger of excessive vibration throughout the exposures. The mechanical pump was connected to a mercury diffusion pump with 10 meters of 14 mm. diameter pyrex tubing. A dry ice-methanol trap was built into the vacuum system at the entrance to the etalon chamber; this trap prevented mercury and water vapor from entering the chamber.

The air pressure in the etalon chamber was measured with a MacLeod gauge. While the pressure was not measured accurately, it was found to be less than one micron of mercury. At that pressure the residual air would produce a change of 0.000002 A at the most in the wavelengths at 6000 A and less in the ultra-violet. Since this is considerably beyond the accuracy of measurement of the wavelengths, the effect of the residual pressure may be neglected.

2. Sources and Excitation.

The neon source was an ordinary Geissler discharge tube. The effective size of the source was limited by an aperature of black paper fitted on the capilliary portion of the tube. The tube was excited by 60 cycle, 110 volts transformed to a potential of 8000 volts. The current through the tube was 7 milliamperes.

The mercury 198 tube was supplied by Baird Associates, Cambridge, Massachusetts. It was constructed of vycor glass and contained a few milligrams of artificially prepared $^{198}_{80}$Hg and a trace of $^{199}_{80}$Hg. A 600 megacycle/sec. war-surplus radar generator was used to excite the discharge. The generator has two triode push-pull, tuned plate-tuned cathode oscillators working in parallel. A detailed description is given by M.I.T. Radar School Staff.(10) According to Tolansky(6) no clean-up of the element in the tube occurs under the electrodes; therefore the tube was wrapped completely in aluminum foil except for the interelectrode space.

3. The Optical System

The light from the discharge tubes, which were viewed transversely (i.e., in a direction perpendicular to their long axis), was condensed by a quartz lens and focussed at a spot approximately halfway between the etalon plates (fig. 2). The discharge tubes were fastened to a sliding holder which allowed them to be alternately positioned in front of the condensing lens. After emerging from the interferometer the light was focussed on the slit of the spectrograph by a quartz-fluorite achromat of focal length 26 cm.

To check that the centre of the interference pattern fell on the slit a small light source was placed in the spectrograph near the prism. The light

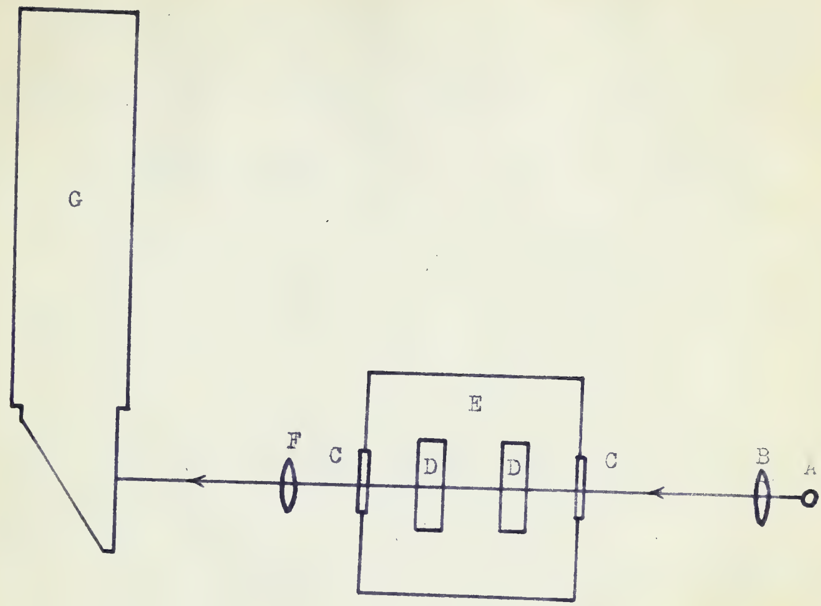

Figure 2. Optical System

A: discharge tube
B: quartz condensing lens
C: optically flat quartz windows
D: etalon plates
E: etalon chamber
F: quartz-fluorite achromat
G: Hilger E 1 Spectrograph

from this source was directed through the slit to the etalon plate and reflected back from the metal surface towards the slit. The etalon was considered perpendicular to the path of the light beam when the reflected light fell back exactly on the slit.

4. <u>The Densitometer.</u>

Analysis of the interference patterns involved the measurement of the distance between corresponding fringes on opposite sides of the centre of the pattern. A densitometer was used to make a trace of the pattern on a paper chart. An ordinary scale was then used to make the necessary measurements.

The densitometer consists essentially of a plate holder moving on a carriage and a device for detecting variations in the image density of the photographic emulsion. The carriage screw which was known to be of high quality, was rotated by the external drive of the Esterline - Angus recording milliameter. A slight change was made in the method of driving the carriage screw. Previously the chart drive and the carriage drive had been connected by a set of fiber gears. Since it was thought that these gears might have small irregularities, an alteration was made so that the carriage and chart were driven from the same shaft. No conclusion could be made as to the consequences of this change, but indications were that the trace of

the pattern was more uniform.

The device for scanning the pattern consisted of a light focussed on the photographic emulsion; from there the light was focussed by another lens on the slit of a photomultiplier tube 931-A. The output of the photomultiplier tube was fed into a 6J5 triode used as a cathode-follower amplifier; the current of this amplifier was measured with the Esterline-Angus recording milliameter.

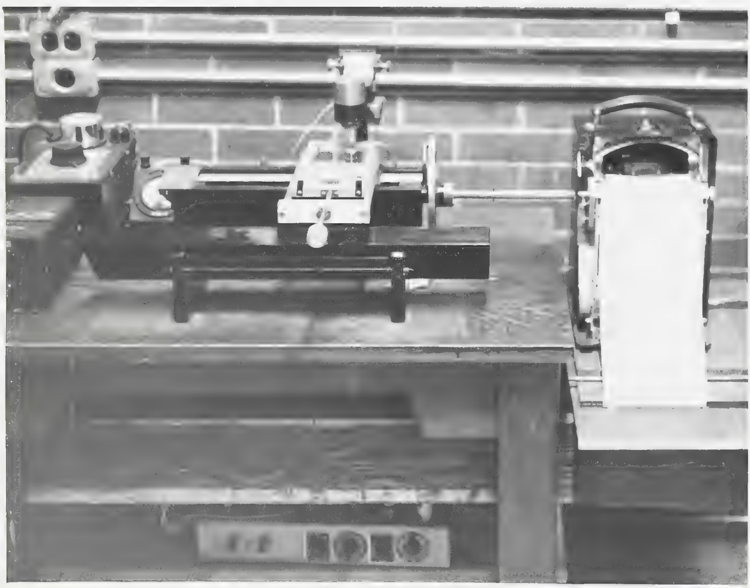

Plate 4. Densitometer.

IV EXPERIMENTAL PROCEDURE

1. Preliminary Adjustments

Several hours before the exposure was begun the temperature control for the water bath was put into operation to permit the etalon to reach temperature equilibrium. After equilibrium had been reached the etalon was checked for parallelism of the plates. This was done by moving a telescope focussed at infinity from side to side and up and down across the face of the etalon plate. If the plates were parallel no difference in the diameter of the interference rings was observed when this was done. In a few cases a slight adjustment was necessary to bring the plates back to parallelism.

After the check for parallelism the etalon chamber was flushed twice with air which had been passed over phosphorus pentoxide and anhydrous sodium hydroxide in order to remove water vapor and carbon dioxide. Finally the chamber was evacuated and the diffusion pump was left in operation for at least one hour before the exposures were begun. After this time the air pressure had been reduced sufficiently and temperature equilibrium had certainly been reached.

2. Vacuum Exposures.

The vacuum exposures were then made on Eastman

Kodak III-F Spectroscopic Plates, which are sensitive from 2000 A to 6900 A, in the following order:

1) Neon, visible, 4 minutes.
2) Mercury, visible, 30 minutes.
3) Mercury, far ultra-violet, 4 minutes.
4) Mercury, ultra-violet, 90 minutes.
5) Neon, visible, 4 minutes.

The temperature and the functioning of the thermostat were checked after each exposure to insure that the temperature had been maintained constant. The air pressure was also checked.

Nine plates were taken, three with each of the etalon spacers.

3. Processing of Plates.

The spectroscopic plates were developed in Kodak D-19 for 8 to 9 minutes depending on the condition of the developer, and fixed in Ansco acid fixer with hardener for 10 minutes. Care was taken to have the developer, fixer and wash water at nearly the same temperature. Finally the plates were washed, rinsed in a wetting agent, and dried in a gentle stream of unheated air blown through oil-soaked cheesecloth to collect the dust from the air. These precautions are necessary to prevent shrinking or expansion of the emulsion during the processing. (6) (13)

V RESULTS AND DISCUSSION

Observations were made with three etalon spacers, 1.5 cm., 2.5 cm., and 2.8 cm. Since no large spacers other than the 1.5 cm. and 2.8 cm. were available, the 2.5 cm. spacing was obtained by placing 1.0 cm. and 1.5 cm. spacers together. The two spacers together tended to be somewhat more unstable than a single spacer. Whereas the single spacers changed about 1 part in 10^8 during the 3 hours necessary for the exposures, the double spacer changed about 4 parts in 10^8 during that time. Nevertheless since this change was of the order of the accuracy possible in the measurement of the plate separation, the results from all three spacers were given equal value.

The data from the nine plates is given in Appendix IV. Four neon lines which had been measured with respect to the primary standard, cadmium 6438.4696 A, were chosen as the secondary standards.[9] The standard wavelengths were converted to vacuum wavelengths by use of the refractive index calculated from the averaged data of Barrell and Sears and of Perard (Appendix III). Eighteen lines of the mercury 198 spectra were measured. Seventeen of these were from mercury in the ground and singly-ionized state; one, the 4705 A line was from the spectrum of doubly-ionized mercury.

Phase change corrections were made by combining the data from the 1.5 cm. and 2.5 cm. and from the 1.5 cm. and 2.8 cm. spacers. The calculations are given in Appendix IV. The corrected wavelengths calculated from the two combinations were averaged to give final values of wavelength. These are shown in Table 1; the standard wavelength is calculated by using the refractive index computed from the averaged data of Barrell and Sears and of Perard. The experimental errors quoted are the standard deviations.

Table 1. Final Vacuum Wavelengths of Mercury 198

Final Vacuum Wavelength (in Angstroms)		Refractive Index $(\mu - 1) \times 10^6$	Standard Air Wavelength
2537.26830	±.00028	300.65	2536.50571
2652.83253	37	297.87	2652.04257
2753.59686	45	295.77	2752.78266
2894.44652	28	293.27	2893.59793
2968.14968	23	292.15	2967.28280
3022.37973	15	291.33	3021.49947
3024.35686	38	291.30	3023.47611
3126.57562	31	289.95	3125.66932
3342.44273	24	287.55	3341.48189
3651.19636	54	284.91	3650.15639
3655.88053	33	284.88	3654.83935
3664.32416	31	284.82	3663.28080
4047.71484	33	282.45	4046.57188
4078.98951	44	282.29	4077.83838
4359.56218	44	281.01	4358.33746
4705.95714	130	279.64	4704.64152
5462.27094	51	277.85	5460.75368
5792.26810	48	277.25	5790.66263

Table 2. Comparison of Results with Other Experimenters.

Standard Wavelength* (in Angstroms)	Present Work**		J.M. Blank[2]	W.F. Meggers and K.G. Kessler[3]	K.Burns and K.B.Adams[4]
2536	.5057	±.0003		.5064	.5063
2652	.0426	4		.0426	.0425
2752	.7827	4		.7827	.7828
2893	.5979	3		.5980	.5982
2967	.2828	2		.2833	.2832
3021	.4995	2		.4997	.4996
3023	.4761	4		.4762	.4764
3125	.6693	3		.6700	.6698
3341	.4819	2		.4814	.4814
3650	.1564	5	.15688	.1567	.1564
3654	.8394	3		.8393	.8392
3663	.2808	3		.2808	.2808
4046	.5719	3	.57161	.5715	.5712
4078	.8384	4		.8379	.8379
4358	.3375	4	.33763	.3376	.3372
4704	.6415	13	——	——	——
5460	.7537	5	.75313	.7532	.7532
5790	.6626	5	.66272	.6626	.6626

* Integral part only

** Columns 2, 3, 4 and 5 contain the fractional part of the wavelength only.

A comparison of the results of the present work with those of previous experimenters is made in Table 2. There is agreement within experimental error for most of the wavelengths. Exceptions are the lines 2537 A, 3126 A, and 3341 A. For these lines the phase change correction as calculated from the 1.5 cm. and 2.5 cm. spacer combination is considerably different from that calculated from the 1.5 cm. and 2.8 cm. spacer combination; since the two combinations are nearly the same, the phase change corrections should also be nearly the same. However this consideration cannot be used as a basis for rejecting the results for these lines. The two phase change corrections differ considerably also for several other lines which do agree well with previous determinations, namely, the lines 3655 A, 3663 A, 4358 A, and 5791 A.

The largest part of the error in calculation is introduced during the application of the phase change correction. As was mentioned previously in the theory of the phase change correction, this error can be kept at a minimum by a proper choice of etalon separations. It would appear that a 0.5 cm. or 1.0 cm. spacer would have been a better choice than the 1.5 cm. spacer. In those cases the probable error in the correction would have been one-third or one-half that of the present work.

Since the lines of the mercury discharge are very sharp, a greater accuracy in measurement should be attainable - J.M. Blank [2], for instance, quotes a standard deviation of

about 0.0001 A in his determination of the wavelengths. A place for possible improvement exists in the measurement of the fractional part of the order number, e. The criterion for accepting the measured value of e was arbitrarily taken to be that the standard error of estimate should be less than 0.0075. It was possible to achieve this accuracy, with one or two exceptions. In many cases it was found that the accuracy was improved by a remeasurement of line; hence it would appear that the manner in which the densitometer itself was operated had some effect on the results of the measurement. The best results were obtained from the more intense lines; the lower limit on the standard error of estimate for these lines appeared to be 0.0010, with most being around 0.0030. It is likely that the values of e would be improved if each line were measured three times, say, and the average result taken.

Appendix 1. Derivation of Normal Equations For The Least Squares Method.

The least squares method provides a useful criterion for computing the best equation relating sets of experimental data.

For an equation of the form

$$y = a + bx + cx^2 + \ldots \qquad (1)$$

there will be values of Ycn corresponding to values of Xn, where Ycn is computed by the equations

$$\begin{aligned} Yc_1 &= a + bX_1 + cX_1^2 + \ldots \\ Yc_2 &= a + bX_2 + cX_2^2 + \ldots \\ &\ldots \\ Yc_N &= a + bX_N + cX_N^2 + \ldots \end{aligned} \qquad (2)$$

The criterion of the least squares method is that the quantity $\sum_{n=1}^{N} (Y_n - Y_{cn})^2$ be a minimum, where Yn is the experimental value of the first set corresponding to the value of Xn of the second set. Application of the criterion results in the equations

$$\begin{aligned} \frac{\partial}{\partial a} \sum_{n=1}^{N} (Y_n - Y_{cn})^2 &= 0 = 2 \sum_{n=1}^{N} (Y_n - a - bX_n - cX_n^2 - \cdots) \\ \frac{\partial}{\partial b} \sum_{n=1}^{N} (Y_n - Y_{cn})^2 &= 0 = 2 \sum_{n=1}^{N} (Y_n - a - bX_n - cX_n^2 - \cdots) X_n \\ &\ldots \end{aligned} \qquad (3)$$

Or, rewriting,

$$\begin{aligned} \sum_{n=1}^{N} Y_n &= Na + b \sum_{n=1}^{N} X_n + c \sum_{n=1}^{N} X_n^2 + \ldots \\ \sum_{n=1}^{N} X_n Y_n &= a \sum_{n=1}^{N} X_n + b \sum_{n=1}^{N} X_n^2 + c \sum_{n=1}^{N} X_n^3 + \ldots \end{aligned} \qquad (4)$$

Equations (4) are the normal equations.

A measure used to indicate the excellence of fit of the least squares equation is the standard error of estimate; it is computed by the relation

$$\text{Standard error of estimate} = \sqrt{\sum_{n=1}^{N} \frac{(Y_n - Y_{cn})^2}{n}} \qquad (5)$$

Appendix 2. Focus Settings of the Hilger Spectrograph

The focus settings of the Hilger El Littrow Spectrograph are not the same for focussing horizontal and vertical lines because of astigmatism in the spectrograph. Since the interference maxima appear as horizontal lines across the slit, settings must be determined which best focus such lines.

For each region of the spectrum the two foci for horizontal and vertical lines are closest to each other for the longer wavelengths. For example, in the region 3400 A - 7000 A the foci are closest together at 7000 A; in the region 2400 A - 3400 A the foci are closest at 3400 A. The foci are considerably closer together for the 3400 A line in the 2400 A - 3400 A region than for that line in the 3400 A - 7000 A region.

The line 2537 A shows appreciable lateral spreading in the region 2400 A - 3400 A; as a result there is an apparent decrease in intensity and the line is diffused. Settings were found for a region 2700 A and less; in that region the 2537 A line appeared much sharper and a shorter exposure was required.

The focus settings were found by test exposures. A brass slide across which were placed a number of fine glass strands was substituted for the fishtail. When the slide was in position the glass strands were very nearly in contact with the spectrograph slit and acted

effectively as sharp horizontal lines. The results are summarized in the table.

Region	Focus	Prism Rotation	Plate Holder Tilt
2400 A and less	24 -17	12.00	16.0
2400 A- 3400A	37 -6	14.83	13.3
3400 A- 7000A	53-15	18.03	5.5

Appendix 3. Refractive Index of Air

The refractive index of air must be known to about 8 or 9 significant figures in order to convert the known standard wavelengths to vacuum wavelengths. The averaged data of Barrell and Sears (11) and of Perard (12) was used. A least squares line of the form

$$\mu - 1 = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (1)$$

was fitted to their data, where A,B, and C are constants. The result is the equation

$$(\mu - 1) \times 10^6 = 272.670 + \frac{1.47353}{\lambda^2} + \frac{0.021010}{\lambda^4}$$

where λ is measured in microns.

The refractive index for the 4 neon lines used as secondary standards are given in the table.

Standard Wavelengths (in Angstroms)	$(\mu - 1) \times 10^6$	Vacuum Wavelengths
5852.4878	277.146	5854.10979
5944.8340	277.003	5946.48074
6217.2812	276.616	6219.00100
6266.4952	276.552	6268.22821

Appendix 4. Observations and Calculations

a. Observations from Vacuum Plates

The observations at the three etalon separations are summarized in tables 1, 2, and 3. The wavelengths which appear in tables 4 and 5 are the weighted averages of the wavelengths calculated in tables 1, 2, and 3. The standard errors of estimate, which are quoted in the tables, were used as a basis for determining the value of a calculation. In no case was any measurement given a weight of more than two as compared to one for the least accurate measurement.

Table 1. Data from 1.5 cm. Spacer.

	Vacuum Wavelength (in Angstroms)	Interference Order Numbers*	Plate 1		Plate 2		Plate3	
			Interference Order Number**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)
Initial Neon Exposure	5854.10979	51,244	.7506	2.99992 396	.7576	2.99992 437	.7559	2.99992 427
	5946.48074	50,448	.7311	408	.7375	446	.7325	416
	6219.00100	48,238	.0336	379	.0373	402	.0305	360
	6268.22821	47,859	.2031	407	.2033	408	.2020	400
				Average: 2.99992 398		Average: 2.99992424	[illegible]	Average: 2.99992 401
Final Neon Exposure	5854.10979	51,244	.7573	2.99992 435	.7616	2.99992 461	.7566	2.99992 431
	5946.48074	50,448	.7346	429	.7345	428	.7354	433
	6219.00100	48,238	.0328	374	.0371	401	.0318	368
	6268.22821	47,859	.1985	378	.2002	389	.1991	382
				Average: 2.99992 404		Average: 2.99992 420		Average: 2.99992 403
				Overall average: 2.99992 404		Overall average: 2.99992 422		Overall average: 2.99992 402

	Vacuum Wavelengths* (in Angstroms)	Interference Order Number*	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)
Mercury Exposure	2537	118,234	.3938 ±.0048	.26848	.3838 ±.0046	.26888	.3865 ±.0052	.26865
	2652	113,083	.7818 29	.83311	.7913 40	.83308	.7812 39	.83314
	2753	108,945	.6340 40	.59728	.6563 60	.59690	.6220 39	.59759
	2894	103,644	.1445 35	.44621	.1457 46	.44638	.1354 23	.44647
	2967	101,070	.5222 32	.14931	.5272 22	.14937	.5143 33	.14956
	3022	99,257	.0236 55	.37958	.0306 29	.37958	.0202 50	.37969
	3024	99,192	.1015 28	.35775	.1236 36	.35729	.1033 56	.35771
	3126	95,949	.2061 17	.57512	.2103 35	.57521	.1976 66	.57541
	3342	89,752	.4675 09	.44182	.4682 25	.44203	.4692 41	.44177
	3651	82,162	.7874 51	.19552	.7886 19	.19572	.7719 53	.19622
	3655	82,057	.5235 32	.87929	.5248 33	.87949	.5170 22	.87960
	3664	81,868	.4276 18	.32347	.4261 13	.32380	.4278 42	.32348
	4047	74,114	.0328 41	.71390	.0367 26	.71397	.0239 24	.71440
	4078	73,545	.7790 58	.98869	.7895 31	.98840	.7724 55	.98907
	4359	68,812	.5049 19	.56228	.5143 26	.56199	.4982 24	.56272
	4705	63,747	.3706 39	.95725	.3602 36	.95835	.3638 56	.95777
	5462	54,920	.8164 27	.27133	.8254 10	.27082	.8226 30	.27073
	5792	51,791	.8755 29	.26757	.8769 35	.26782	.8793 15	.26717

*Integral part only.
**Fractional part only.

Table 2. Data From The 2.5 cm. Spacer.

	Vacuum Wavelengths (in Angstroms)	Interference Order Number*	Plate 4		Plate 5		Plate 6	
			Interference Order Nmmber**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)
Initial Neon Exposure	5854.10979	85,412	1.0225	5.00017 211	.9863	5.00016 999	.9876	5.00017 007
	5946.48074	84,086	.2336	169	.1997	967	.2156	062
	6219.00100	80,401	.5293	191	.4972	991	.5001	010
	6268.22821	79,770	.1038	215	.0703	5.00017 005	.0781	054
				Average: 5.00017 196		Average: 5.00016 990		Average: 5.00017 033
Final Neon Exposure	5854.10979	85,412	1.0157	5.00017 171	.9901	5.00017 022	.9895	5.00017 018
	5946.48074	84,086	.2292	142	.2063	006	.2085	019
	6219.00100	80,401	.5220	146	.4979	5.00016 996	.4979	5.00016 996
	6268.22821	79,770	.1016	201	.0752	5.00017 036	.0749	5.00017 034
				Average: 5.00017 165		Average: 5.00017 015		Average: 5.00017 017
				Overall average: 5.00017 181		Overall average: 5.00017 003		Overall average: 5.00017 025

	Vacuum Wavelength* (in Angstroms)	Interference Order Number*	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)
Mercury Exposure	2537	197,069	.0756 ±.0030	.26862	$\bar{1}$.9970 ±.0025	.26873	.0028 ±.0044	.26876
	2652	188,484	.2127 52	.83322	.1635 140	.83297	.1977 67	.83260
	2753	181,586	.9011 60	.59719	---- --	-----	.8367 128	.59731
	2894	172,750	.5214 56	.44672	.4531 67	.44684	.4909 50	.44633
	2968	168,460	.9078 55	.14963	.8420 74	.14973	.8624 60	.14950
	3022	165,438	.2364 36	.37978	.1668 37	.37998	.1869 27	.37974
	3024	165,330	.0543 31	.35745	---- --	-----	.0193 30	.35714
	3126	159,924	.8698 42	.57551	.7971 67	.57582	.8125 51	.57565
	3342	149,596	.3355 53	.44271	.2861 50	.44262	.3033 40	.44239
	3651	136,946	.1287 31	.19617	.0738 31	.19634	.0991 18	.19582
	3655	136,770	.6747 40	.88005	.6146 28	.88035	.6312 12	.88007
	3664	136,455	.5008 15	.32411	.4435 28	.32434	.4609 32	.32403
	4047	123,530	.7440 44	.71448	.6954 17	.71463	.7081 33	.71439
	4078	122,583	.5970 45	.98930	---- --	-----	.5694 03	.98895
	4359	114,694	.3448 20	.56264	.3043 45	.56263	.3171 24	.56234
	4705	106,251	.9496 58	.95771	.---- --	------	.9512 61	.95617
	5462	91,540	.1650 16	.27092	.1295 10	.27109	.1399 25	.27071
	5792	86,324	.9408 41	.26787	.---- --	-----	.9125 50	.26796

*Integral part only.
**Fractional part only.

Table 3. Data From The 2.8 cm. Spacer.

	Vacuum Wavelength (in Angstroms)	Interference Order Number*	Plate 7		Plate 8		Plate 9	
			Interference Order Number**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)	Interference Order Number**	Double Plate Separation (in cm.)
Initial Neon Exposure	5854.10979	95,634	.4099	5.59854 355	.4237	5.59854 416	.4189	5.59854 388
	5946.48074	94,148	.8565	362	.8670	424	.8604	385
	6219.00100	90,023	.2035	393	.2058	407	.2115	442
	6268.22821	89,316	.2154	421	.2085	378	.2214	459
				Average: 5.59854 378		Average: 5.59854 406		Average: 5.59854 418
Final Neon Exposure	5854.10979	95,634	.4192	5.59854 390	.4206	5.59854 398	.4151	5.59854 366
	5946.48074	94,148	.85133	331	.8638	405	.8617	393
	6219.00100	90,023	.2061	409	.2088	426	.2114	442
	6268.22821	89,316	.2088	380	.2118	398	.2158	423
				Average: 5.59854 378		Average: 5.59854 407		Average: 5.59854 406
				Overall average: 5.59854 378		Overall average: 5.59854 406		Overall average: 5.59854 412
	Vacuum Wavelength* (in Angstroms)	Interference Order Number*	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)	Interference Order Number**	Vacuum Wavelength** (in Angstroms)
Mercury Exposure	2537	220,652	.4112 ±.0052	.26834	.4146 ±.0075	.26843	.4479 ±.0066	.26808
	2652	211,040	.2248 72	.83255	.2223 59	.83272	.2023 70	.83300
	2752	203,317	.4531 22	.59724	.4827 41	.59698	.5013 13	.59676
	2894	193,423	.6542 62	.44629	.6600 75	.44635	.6620 74	.44635
	2968	188,620	.6961 71	.14925	.6875 30	.14954	.7001 58	.14936
	3022	185,236	.2942 58	.37950	.3051 53	.37947	.2998 ±.0030	.37959
	3024	185,115	.1614 38	.35724	.1726 60	.35720	.1912 77	.35693
	3126	179,063	.1502 69	.57505	.1396 59	.57539	.1652 33	.57498
	3342	167,498	.6048 29	.44204	.6221 36	.44186	.6135 21	.44207
	3651	153,334	.5331 75	.19564	.5219 53	.19608	.5202 26	.19616
	3655	153,138	.0638 40	.87996	.0804 48	.87974	.0932 27	.87948
	3664	152,785	.1864 52	.32369	.1997 56	.32355	.2100 12	.32335
	4047	138,313	.7049 32	.71442	.7184 42	.71423	.7236 50	.71412
	4078	137,253	.2242 31	.98890	.2257 56	.98906	.2316 20	.98893
	4359	128,419	.8720 29	.56188	.8733 13	.56205	.8796 14	.56188
	4705	118,967	.1518 58	.95765	.1317 37	.95868	.1712 43	.95717
	5462	102,494	.7975 37	.27118	.8127 40	.27064	---- --	-----
	5792	96,655	.4710 32	.26786	.4870 26	.26719	.4845 29	.26740

*Integral part only.
**Fractional part only.

b. Phase Change Correction

Table 4. Correction for 1.5 cm. and 2.5 cm. Spacers

Vacuum Wave-length* (in Angstroms)	Wavelength** at 1.5 cm. Spacer		Wavelength** at 2.5 cm. Spacer		Phase Change Correction to 2.5 cm. Spacer		Corrected Wavelength**	
2537	.26867	±.00016	.26871	±.00006	+.00006	±.00026	.26876	±.00027
2652	.83311	2	.83292	26	-.00028	39	.83264	46
2753	.59730	29	.59723	5	10	44	.59713	44
2894	.44638	11	.44663	22	+.00038	38	.44701	44
2968	.14941	11	.14962	10	32	22	.14994	23
3022	.37961	5	.37983	10	33	16	.38016	19
3024	.35751	22	.35730	16	-.00032	40	.35698	43
3126	.57521	13	.57564	14	+.00064	28	.57628	31
3342	.44188	11	.44257	14	104	27	.44361	30
3651	.19580	30	.19607	22	40	56	.19647	59
3655	.87948	13	.88014	14	99	28	.88113	31
3664	.32360	15	.32415	13	82	30	.32497	33
4047	.71412	22	.71453	10	62	34	.71515	35
4078	.98864	29	.98907	15	64	50	.98971	52
4359	.56233	30	.56254	14	32	50	.56286	52
4705	.95779	45	.95694	77	-.00128	134	.95566	160
5462	.27092	27	.27095	16	+.00004	46	.27099	49
5792	.26743	28	.26792	5	74	42	.26866	42

*Integral part only
**Fractional part only

Table 5. Correction for 1.5 cm. and 2.8 cm. Spacers

Vacuum Wave-length* (in Angstroms)	Wavelength** at 1.5 cm. Spacer		Wavelength** at 2.8 cm. Spacer		Correction to 2.8 cm. Spacer		Corrected Wavelength**	
2537	.26867	±.00016	.26828	±.00015	-.00045	±.00025	.26783	±.00029
2652	.83311	2	.83276	19	40	22	.83236	29
2753	.59730	29	.59697	20	38	40	.59659	45
2894	.44638	11	.44633	03	06	13	.44627	13
2968	.14941	11	.14942	12	+.00001	18	.14943	22
3022	.37961	5	.37953	06	-.00009	09	.37944	11
3024	.35751	22	.35715	14	42	30	.35673	33
3126	.57521	13	.57510	18	13	25	.57497	31
3342	.44188	11	.44200	09	+.00014	16	.44214	18
3651	.19580	30	.19601	22	24	43	.19625	48
3655	.87948	13	.87969	20	24	28	.87993	34
3664	.32360	15	.32348	15	-.00014	24	.32334	29
4047	.71412	22	.71427	12	+.00017	29	.71454	31
4078	.98864	29	.98895	07	36	35	.98931	35
4359	.56233	30	.56195	08	-.00044	36	.56151	37
4705	.95779	45	.95795	65	+.00018	91	.95813	110
5462	.27092	27	.27091	27	-.00001	44	.27090	52
5792	.26743	28	.26748	28	+.00006	45	.26754	53

* Integral Part Only

** Fractional Part Only

BIBLIOGRAPHY

1. Weins and Alvarez, Phys. Rev. 58, 1005 (1940).

2. J.M. Blank, Jour. Optical Soc. Am. 40, 337 (1941)

3. Meggers and Kessler, Jour. Opt. Soc. Am. 42, 737 (1950)

4. Burns and Adams, Jour. Opt. Soc. 42, 56 (1952)

5. K.W. Meissner, Jour. Optical Soc. Am. 31, 405 (1941).

6. S. Tolansky, High Resolution Spectroscopy, Pitman (1947).

7. A.W. Smith, Precision Determination of Argon Wavelengths in the Region 3900 A to 4600 A, Unpublished Master's Thesis, Library, University of Alberta (1952).

8. R.A. Olafson, Ultra-Violet Dispersion of Air, Unpublished Master's Thesis, Library, University of Alberta (1955).

9. Handbook of Chemistry and Physics, 32nd Ed., Chemical Rubber Publishing Co. (1950-51).

10. M.I.T. Radar School Staff, Principles of Radar, McGaw-Hill (1948).

11. Barrell and Sears, Trans. Roy. Soc. (London) A 238, 1 (1939).

12. Perard, Trav. Bur. Int. Pds. Mes., 19, 78 (1934).

13. Procedures in Experimental Physics, J. Strong. Prentice Hall, (1946)

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